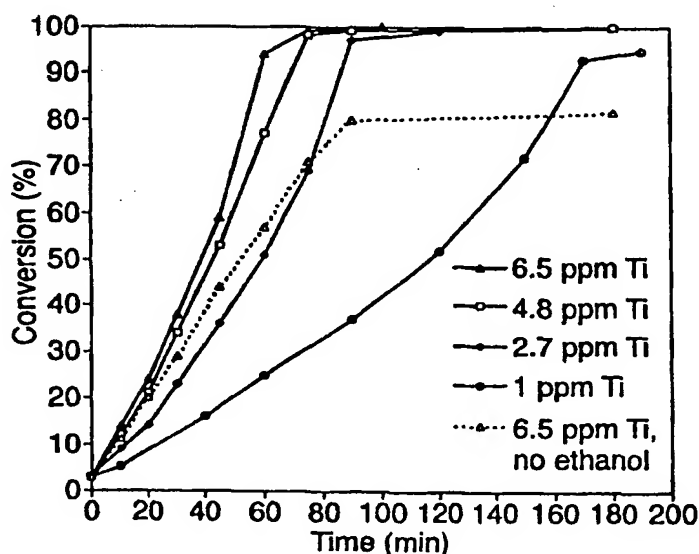




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : B01J 31/00		A2	(11) International Publication Number: WO 00/25915
			(43) International Publication Date: 11 May 2000 (11.05.00)
(21) International Application Number: PCT/EP99/08311		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 28 October 1999 (28.10.99)			
(30) Priority Data: 98308932.7 30 October 1998 (30.10.98) EP			
(71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).			
(72) Inventors: VAN DER HEIJDEN, Harry; Badhuisweg 3, NL-1031 CM Amsterdam (NL). VAN DE WEG, Hendrik; Badhuisweg 3, NL-1031 CM Amsterdam (NL).		Published Without international search report and to be republished upon receipt of that report.	

(54) Title: A METHOD FOR PREPARING A HYDROGENATION CATALYST SYSTEM



(57) Abstract

This invention concerns a method for preparing a hydrogenation catalyst system process involving the reaction of a group 4 metallocene (A) with a metal hydride or an organometallic compound (B) at a (B)/(A) molar ratio that is larger than 10 followed by the activation of the resulting catalyst mixture with hydrogen at a hydrogen pressure p (in MPa) and at a temperature T (in °C), wherein a neutralising agent (C) that is capable of reacting with the compound (B) is added to the catalyst mixture: (a) either prior to the activation; b) within t hours from the activation wherein t equals x divided by $(p * T * (B)/(A))$, and x corresponds to 10,000, and a process for the hydrogenation of an olefinically unsaturated compound with hydrogen in the presence of a hydrogenation catalyst system obtained by the method of the invention.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

A METHOD FOR PREPARING A HYDROGENATION CATALYST SYSTEM

Field of the invention

This invention concerns a method for preparing a hydrogenation catalyst system process, and a process for the hydrogenation of an olefinically unsaturated compound with hydrogen in the presence of a hydrogenation catalyst system obtained by the method of the invention.

Background of the Invention

US 3663635, DE 3401983, US 5039755, US 5132372, EP 339986, EP 434469, EP 544304, EP 795564, EP 810231, and WO 9525130 described catalyst systems for the hydrogenation of olefinically unsaturated compounds, and in particular for the hydrogenation of conjugated diene (co)polymers. These catalyst systems are prepared by reacting a titanocene or similar group 4 metallocene (A) (i.e., a ferrocene-like molecule based on a group 4 metal and 2 η^5 ligands), with a metal hydride or an organo-metallic compound (B) and contacting (activating) the resulting catalyst mixture with hydrogen. These catalyst systems have a very high hydrogenation activity.

US 3663635, for instance, describes catalyst systems for the hydrogenation of unsaturated compounds such as olefins based on titanocenes of the formula TiX_2Y_2 in which X represents halide, amino, hydrocarbylamino, thio, carboxylate, alkoxide or a hydrogen atom, and Y is cyclopentadienyl, indenyl, fluorenyl or allyl substituted or not, which are reacted with an aluminium hydride.

DE 3401983 describes catalyst systems for the hydrogenation of (co)polymers of conjugated dienes based on titanocenes of the formula $(C_5H_5)_2TiRR'$ wherein R and R' may be the same or different, representing a C_1 - C_8 alkyl

or alkoxy group; C₆-C₈ aryl, aryloxy, aralkyl- or cycloalkyl group; a halogen atom or a carbonyl group, which are reacted with a lithium compound, i.e., a living (polybutadiene) polymer.

5 US 5039755 describes the hydrogenation of a conjugated diene (co)polymer that is terminated with hydrogen in the presence of a titanocene to which sec-butyl lithium is added.

10 US 5132372 concerns the use of methyl benzoate as promoting agent in titanocene-based hydrogenation reactions. Further promoters are disclosed in US5173537 (which describes the deactivation of lithium hydride by addition of various reagents prior to hydrogenation and titanium catalyst addition).

15 EP 339986 concerns hydrogenation catalyst systems consisting of at least one titanocene and a lithium compound in a molar ratio of 1/0.5 to 1/20, and optionally a reducing organometallic compound selected from the group consisting of aluminium compounds, zinc compounds and magnesium compounds.

20 EP 434469 describes a hydrogenation catalyst system based on at least one group 4 metallocene, at least one complex lithium, sodium or potassium compound, and optionally a polar compound or an alkali oxyhydrocarbyl compound.

25 EP 544304 describes a hydrogenation catalyst system based on at least one group 4 metallocene, at least one polarized compound selected from the group consisting of carbonyl group-containing compounds and epoxy group containing compounds, and an organic lithium compound.

30 Ligand variations have been subject of study as well. For instance, EP 795564 describes a catalyst composition based on indenyl or an indenyl-like compound as ligand, whereas EP 810231 describes catalyst systems based on

heterocyclic (phosphorus containing) cyclopentadienyl-like compounds as ligand.

A zirconium-based hydrogenation catalyst system is described in WO 9525130.

5 Unfortunately, the activity of these catalyst systems strongly depends on a proper molar ratio of (B) over (A). It is common practice in the above documents to specify a molar ratio of (B)/(A) in the range of, e.g., 2 to 20 (e.g., DE 3401983). However, the actual operating window
10 illustrated in the art is much narrower than this. Typically the (B)/(A) ratio at which adequate hydrogenation is achieved is in the range of 5 to 10. Apparently, at lower ratios the metallocene is insufficiently activated. At higher ratios the catalyst
15 systems are less effective, believed to be due to increased catalyst decay. This is particularly unfortunate if the metal hydride or organometallic compound (B) is already present in high amounts in the olefinically unsaturated compounds to be hydrogenated.

20 It will therefore be appreciated that there is a need for an improved catalyst preparation method and an improved hydrogenation process.

 From JP 8033846 a catalyst preparation method is known wherein a storage stable catalyst system is
25 prepared by reacting the titanocene (A) with an organometallic compound (B) in the presence of a polymer containing olefinic unsaturated double bonds. The resulting catalyst mixture is in direct contact with hydrogen, and to this a polar compound is added.

30 The catalyst system of this Japanese patent document is produced separately from the olefinically unsaturated compound. Optimising the (B)/(A) ratio will therefore be less of a problem. Moreover, should the catalyst system should suffer from catalyst decay during hydrogenation,

then additional catalyst may be withdrawn from storage and added to the hydrogenation reaction.

However, although the problem of catalyst decay would appear to be circumvented, it is not solved. Besides, if the catalyst system is to be used for the hydrogenation of a solution containing freshly prepared diene (co)polymers, than organometallic compounds still present therein need to be destroyed first to ensure the optimal (B)/(A) ratio (about 8) is maintained.

The present invention accordingly aims at providing a method for preparing a more robust catalyst system, i.e., that suffers less from catalyst decay, can be prepared in situ and at conventional but also higher (B)/(A) ratios and has increased hydrogenation activity.

As a result of extensive research and experimentation the aim of the present invention is surprisingly achieved by the catalyst preparation method disclosed in claim 1.

Summary of the invention

Accordingly, a method is provided for preparing a hydrogenation catalyst system involving the reaction of a group 4 metallocene (A) with a metal hydride or an organometallic compound (B) at a (B)/(A) molar ratio that is larger than 10 followed by the activation of the resulting catalyst mixture with hydrogen at a hydrogen pressure p (in MPa) and at a temperature T (in °C), wherein a neutralising agent (C) that is capable of reacting with the compound (B) is added to the catalyst mixture -

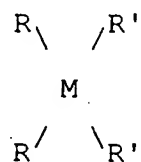
- a) either prior to the activation, or
- b) within t hours from the activation wherein t equals x divided by $(p * T * (B)/(A))$, and x corresponds to 10,000.

Also, a process is provided for the hydrogenation of an olefinically unsaturated compound with hydrogen in the

presence of a hydrogenation catalyst system obtained by the method described above.

Detailed description of the invention

The group 4 metallocene (A) may be any of the
5 metallocenes mentioned in documents mentioned above. Such compounds may be represented by the following general formula:



in which each R represents the same or a different
substituted or unsubstituted, fused, and/or heterocyclic
10 cyclopentadienyl-like η^5 ligand; each R' represents the same or a different group selected from C₁-C₁₂ hydrocarbyl groups, C₁-C₁₂ hydrocarboxyl groups, a carbonyl group, a beta-diketone coordination group or -preferably- a halogen atom, and M is a titanium, zirconium or hafnium
15 atom.

M is preferably a titanium atom. Suitable examples of R include the heterocyclic cyclopentadienyl-like η^5 ligands disclosed in EP 810231, and/or the fused ring system -such as indenyl or fluorenyl- disclosed in
20 US 3663635 and EP 795564. Preferably, both groups R are the same and represent a cyclopentadienyl group.

Suitable substituents, in case one or both groups R are substituted, include halogen atoms, hydrocarbyl groups and/or hydrocarbyloxy groups of up to 12 carbon
25 atoms.

The expressions hydrocarbyl and hydrocarboxyl used above include alkyl and alkoxy groups (cyclic, linear or branched); aryl and aryloxy groups and substituted variants thereof.

Preferably each R' is a halogen atom, more preferably a chloride atom. Therefore, the most preferred group 4 metallocene is bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2).

5 The metallocene is used in amounts of from 0.1 to 500, typically from 1 to 100 mg per kg of unsaturated compound, and preferably in amounts in the range of from 5 to 50 mg/kg. More may be used to speed up the hydro-
10 genation process, but also -given the increased activity of the catalyst system- less may be used, to reduce the cost and environmental impact of the catalyst system.

 The more common organometallic compound used as compound (B), at least in respect of the hydrogenation of (co)polymers of conjugated dienes, are lithium compounds
15 and/or lithium hydride. Examples of the lithium compounds include the living polymer produced using a lithium-based polymerization initiator and added organic lithium compounds such as alkyllithium. Suitable organic lithium compounds are, for instance, listed in EP 544304.

20 In case of the hydrogenation of (co)polymers of conjugated dienes, the lithium hydride may be suitably produced by terminating the lithium-based initiated polymerization by the addition of hydrogen. Since the
25 living polymer and the lithium hydride are readily available, they are preferred.

 However, compound (B) may also be selected from the group organometallic compounds mentioned in JP 8033846, e.g., Na-, K-, Mg-, Ba-, Zn-, Al- or Ca-containing compounds having reducing activity or in any of the other
30 patent documents mentioned herein before.

 The initial molar ratio of compound (B) over group 4 metallocene (A) may vary widely. In contrast to the patent documents mentioned in this specification, there is no upper limit to this ratio. Thus, in the prior art
35 processes the ratio is limited to for instance: 3-30

(US 5039755; US 5132372; US 5242986; EP 532099); 6-25 (EP 795564; EP 801079; EP 810231); 0.5-20 (EP 339986; EP 434469); 2-20 (DE 3401983); 5-15 (US 5244980); less than 15 (EP 601953) or less than 6 (US 5173537). A

5 (B)/(A) ratio in the present process of less than 1000 will most definitely activate all of the metallocene, without poisoning the catalyst system as would occur in the prior art processes. The preferred lower limit (based on economical factors) is at least 15, more preferably at
10 least 20. Suitably, the (B)/(A) molar ratio is in the range of 20-500, more preferably in the range of 25-200, e.g., in the range of 25-100.

The reaction with the metallocene (A) is relatively straightforward. The metallocene is either dissolved in a
15 suitable, inert solvent to which subsequently compound (B) is added or vice versa. No specific pressure and temperature conditions apply. For instance, the metallocene (A) and compound (B) may be reacted by contacting these components for about 1 to 60 minutes,
20 preferably for 5 to 20 minutes at a temperature in the range of 20-90 °C and at a pressure in the range of 0.0 to 5.0 MPa.

The nature of the neutralisation agent (C) depends on the nature of compound (B). Other relevant factors
25 affecting the choice of neutralisation agent are for instance its environmental impact, and its impact on the product qualities and ease of handling.

Suitable neutralisation agents include for instance the compounds mentioned in JP 8083346, e.g., selected
30 from ketone compounds, sulfoxide compounds, carboxylic acid compounds, carboxylate ester compounds, aldehyde compounds, lactone compounds, lactam compounds, amine compounds, amide compounds, nitrile compounds, epoxy compounds and oxime compounds, and the polarized
35 compounds mentioned in EP 0544304. Good results have been

found using aliphatic and/or aromatic alcohols, for instance, lower alkyl alcohols (C_1 to C_6), and optionally substituted phenols. Very good results have been found with the use of ethanol.

5 Preferably, neutralising agent (C) is added to the catalyst mixture formed by the reaction of metallocene (A) with compound (B) before activation. In other words, metallocene (A) and compound (B) are reacted in an inert (hydrogen-free) environment, neutralising agent (C) is
10 added, and then the catalyst mixture is activated with hydrogen.

 However, at temperatures at or below 25 °C and pressures at or below 1 MPa catalyst decay is still relatively insubstantial. Neutralising agent (C) may
15 therefore be added within, for instance, 3 hours from activating the catalyst intermediate without adversely affecting its performance. Indeed, even longer periods may be contemplated, if the temperature and/or pressure is low enough.

20 At temperatures above 25 °C or pressures above 1 MPa catalyst decay will increasingly effect the catalyst performance. The beneficial effects of the present invention may still be achieved if the neutralising agent (C) is added within t hours, wherein t equals x
25 divided by $p * T * (B)/(A)$, and x corresponds to 10,000, preferably 7,500, more preferably 5,000. For instance, at temperatures within 50 to 90 °C and hydrogen pressures above 1 MPa, neutralising agent (C) is added within 15 minutes from activating the catalyst mixture.

30 The presence of metal hydride or organometallic compound (B) and -more importantly- of neutralising agent (C) during the subsequent hydrogenation process is preferably avoided. In other words, the amount of (C) should be sufficient to consume a substantial part of

compound (B) remaining after reaction with metallocene (A). Preferably, neutralising agent (C) is used in a molar ratio of (C)/(B) in the range of 0.1 to 1.05, more preferably in a range of 0.45 to 1.0, e.g., most preferably in the range of 0.5 to 0.9, say in an amount of about 0.6.

The neutralisation of excess compound (B) is relatively straightforward as well. For instance, if the catalyst mixture is a solution comprising the olefinically unsaturated compound and the reaction product of metallocene (A) with compound (B), then neutralising agent (C) may be simply added to that solution. Again, no specific pressure and temperature conditions apply. The neutralisation reaction of compound (B) with agent (C) may for instance be carried out at the conditions described with respect to the reaction of metallocene (A) with compound (B).

The catalyst system may comprise other components, such as the various promoters mentioned in the referred documents.

Like in US 3663635, the catalyst may be used for the hydrogenation of olefinically unsaturated compounds. However, they are preferably used in the hydrogenation of polymers. Polymers that can be hydrogenated by the process of the invention have been described in the various patent documents referred to in the present specification. Of particular interest are polymers of conjugated dienes such as 1,3-butadiene and/or isoprene and copolymers (random or block) of these dienes with vinylaromatic monomers, e.g. with styrene. The process may be used to hydrogenate high and low molecular weight polymers.

The catalyst system has been found to show excellent activity and stability, whereas it is now much more easy

to achieve full hydrogenation at even less than ideal conditions.

The hydrogenation process can be performed at partial hydrogen pressures in the range of from 0.1 to 10 MPa, and preferably from 0.1 to 5.0 MPa.

Preferably, the unsaturated compound to be hydrogenated is diluted with and/or dissolved in a solvent.

Hydrocarbon solvents used in the hydrogenation reaction may be aliphatic hydrocarbons, e.g., pentane, hexane, heptane, octane, etc.; alicyclic hydrocarbons, e.g., cyclopentane, methyl cyclopentane, cyclohexane, etc., or an aromatic solvent such as toluene. These hydrocarbon solvents may contain 20% by weight or a smaller amount of ethers such as diethyl ether, tetrahydrofuran, dibutyl ether, diethoxypropane, dioxane.

Olefinically unsaturated polymers are typically hydrogenated whilst dissolved in a hydrocarbon solvent, for instance the solvent in which the polymer is produced. Usually, the polymer concentration is 1-30% by weight, and preferably 3-20% by weight.

The hydrogenation reaction is effected by supplying hydrogen, with or without stirring, while maintaining the temperature of the (dissolved) unsaturated compound at a specified temperature.

The temperature suitable for the hydrogenation reaction is 0 to 150 °C. A temperature lower than 0 °C is uneconomical, since the rate of hydrogenation is retarded. If the temperature is higher than 150 °C, on the other hand, side-reactions and/or decompositions may occur. Moreover aromatic rings will be hydrogenated at the same time leading to a poor hydrogenation selectivity if only olefinically unsaturated bonds are to be hydrogenated. A more preferable temperature range is 20

to 140 °C, and particularly preferably 50 to 130 °C. The hydrogenation reaction is carried out for a time period of from 1 minute to 3 hours. The reaction time may be shorter when a larger amount of the catalyst composition is used and the pressure is higher.

The invention will now be illustrated by means of the following examples. In these examples, all hydrogenation experiments, unless otherwise indicated, were performed at 5.0 MPa hydrogen, and run for 3 hours, during which period samples were drawn from the reactor and analysed by ¹H NMR to determine the conversion of the olefinic double bonds. Unless otherwise indicated, the Cp₂TiCl₂ catalyst precursor used in the examples was suspended in ONDINA 68 oil (2.5 wt% suspension in oil) (ONDINA is a trade mark).

Example 1 Preparation of hydrogen terminated SBS block copolymer.

A 30 l batch of polystyrene-polybutadiene-polystyrene (SBS) block copolymer of 110,000 molecular weight was prepared in a stainless steel reactor by sequential anionic polymerisation using sec-butyllithium as the initiator. The polymerisation was conducted in cyclohexane (CyC6) at 20 wt% solids, to which was added 140 ppm of diethoxypropane. The vinyl content of the SBS polymer was 40 percent. The polymer contained 30% styrene. At the end of the polymerisation the reactor was sparged with 0.3 MPa of hydrogen for 2 hours to terminate the living SBS-Li polymer and produce a cement composed of SBS and LiH dissolved in CyC6. The LiH content of the polymer cement was determined to be 2.4 mmol/litre.

Comparative Example 2-4 Hydrogenation of SBS block copolymer with bis(cyclopentadienyl) titanium dichloride.

A stainless steel reactor was charged with 800 grams of SBS cement, prepared as described in Example 1. The

temperature of the reactor was fixed at 50 °C and the reactor was pressurised to 0.2 MPa of hydrogen to saturate the cement. Meanwhile a suspension of 42 mg (0.169 mmol, 10 ppm of Ti on cement) of bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2) in 10 ml of CyC6 was prepared. The catalyst suspension was added to the reactor and the hydrogen pressure was raised to 5.0 MPa. Immediately an exothermic reaction occurred.

Following the same procedure two more runs were carried out with 6.5 ppm and 1.0 ppm of Ti on cement.

The results are summarised in Table 1 and Figure 1. From these results, it may be concluded that when in a conventional process LiH to titanium ratio's above 13 are applied, catalyst decay becomes important and no full conversion of the olefinic bonds can be reached.

Table 1: conversion data as a function of titanium levels on cement

Example	ppm Ti on cement	LiH/Ti	15 min conv. (wt%)	60 min conv. (wt%)	180 min conv. (wt%)
C-2	10	13	43	87	98
C-3	6.5	20	29	57	82
C-4	1.0	140	7	7	7

Example 5 Hydrogenation of SBS block copolymer with Cp_2TiCl_2 . Part of the LiH is consumed after the activation of the catalyst

Following the same procedure as described in example 2-4 an experiment was carried out with 27.3 mg (0.110 mmol, 6.5 ppm of Ti on cement) of Cp_2TiCl_2 . After addition of the catalyst suspension to the reactor the catalyst suspension and the SBS cement was mixed for 10 minutes. Then 90 mg of ethanol (1.95 mmol,

0.9 equivalent towards the remaining LiH) dissolved in 10 ml of CyC6 was added to the cement. The hydrogen pressure was raised to 5.0 MPa. Immediately an exothermic reaction occurred.

5 The results are compared with example 3 in Table 2 and Figure 2. In conclusion, a reduction of the LiH to titanium ratio resulted in a more stable hydrogenation catalyst.

Table 2: conversion data as a function of LiH neutralisation using 6.5 ppm of Ti on cement

Example	ethanol addition (a)	LiH/Ti before EtOH	LiH/Ti after EtOH	60 min conv. (wt%)	100 min conv. (wt%)	180 min conv. (wt%)
C-3	0 (b)	20	20	57	81	82
5	0.9	20	2	94	99	100

(a)- equivalent of ethanol towards remaining LiH

(b)- the deactivation procedure, as in US-A-5173537 resulted in a 180 min. conversion of only 30 wt%

10 Example 6-8 Hydrogenation of SBS block copolymer with Cp_2TiCl_2 . Part of the LiH is consumed after the activation of the catalyst

Following the same procedure as described in example 5 experiments were carried out with 19.9 mg, 11.3 mg, and 4.2 mg of Cp_2TiCl_2 .

15 The results are compared with example 3 and 5 in Table 3 and Figure 3. In conclusion, decay of the active hydrogenation catalyst derived from Cp_2TiCl_2 is circumvented when the Li is present as LiOEt. Also, nearly full conversion is achieved within 3 hours with only a fraction of the Ti required when the conventional
20 process is applied.

Table 3: conversion data as a function of LiH neutralisation using various levels of Ti on cement

Example	ppm Ti on cement	ethanol addition (a)	LiH/ Ti before EtOH	LiH/ Ti after EtOH	60 min conv. (wt%)	100 min conv. (wt%)	180 min conv. (wt%)
C-3	6.5	0	20	20	57	81	82
5	6.5	0.9	20	2	94	99	100
6	4.8	0.87	30	4	77	99	100
7	2.7	0.84	53	8.5	52	97	99
8	1.0	0.85	140	22	26	43	95

(a) - equivalent of ethanol towards remaining LiH

Example 9-16 Hydrogenation of SBS block copolymer with Cp_2TiCl_2 . The amount of ethanol to consume (part of) the remaining LiH was varied

Following the same procedure as described in example 5 experiments were carried out with 4.2 mg of Cp_2TiCl_2 . After the preparation of the catalyst intermediate (part of) the remaining LiH was neutralised by reaction with ethanol. The hydrogenation experiments were conducted at 60 °C. The results are summarised in Table 4 and Figure 4.

Table 4: conversion data as a function of the neutralisation of the remaining LiH using 1 ppm of titanium on cement

Example	ethanol addition (a)	LiH/Ti after EtOH	60 min conv. (wt%)	100 min conv. (wt%)	180 min conv. (wt%)
C-9	0	140	7	7	7
10	0.29	100	32	48	66
11	0.45	73	60	99	99.6
12	0.64	47	58	98	98.6
13	0.83	22	58	97	97.7
14	1.01	0	54	97	97.2
C-15	1.15	-	15	15	15
C-16	1.5	-	7	7	7

(a) equivalent of ethanol towards remaining LiH

Examples 17-18 Hydrogenation of SBS block copolymer with Cp_2TiCl_2 . The titanium loading was further reduced applying a neutralisation of LiH with ethanol.

Following the same procedure as described in example 5 experiments were carried out with 2.1 mg and 0.8 mg of Cp_2TiCl_2 . After the preparation of the catalyst intermediate 45 per cent of the remaining LiH was neutralised by reaction with ethanol. The results are compared with example 11 in Table 5.

Table 5: Experimental data of hydrogenation experiments at 1, 0.5 and 0.2 ppm of titanium on cement

Example	ppm Ti on cement	hydro. Temp. (°C)	LiH/Ti at start	after EtOH addition(a)		end conv. (wt%)
				LiH/Ti	EtOH/Ti	
11	1	60	138	73	63	99.6
17	0.5	70	280	150	130	99
18	0.2	80	760	420	350	96

(a) 45 per cent of the remaining LiH is neutralised by reaction with ethanol

It is possible to start hydrogenation experiments at LiH to Ti ratios of even 760 (example 18). After the ethanol addition this ratio is still 420! Full conversion (99 %+) was obtained at ratio's of 73 to 150 after the ethanol addition (examples 11 and 17). Before the invention a ratio of 13 or higher already causes problems. Notice the high ethanol (or LiOEt) levels, which do not matter. Very high LiH levels are acceptable in the polymer cement.

Examples 19-23 Hydrogenation of SBS block copolymer with Cp_2TiCl_2 . The activation time before the ethanol addition was varied.

Following the same procedure as described in example 5 experiments were carried out with 4.2 mg of Cp_2TiCl_2 . After various activation times, 75 per cent of the remaining LiH was neutralised by reaction with ethanol. The hydrogenation experiments were carried out at 70 °C. The results are summarised in Table 6 and Figure 5.

The hydrogenation profiles show only small differences. Already, after one minute activation the catalyst is active and gives a good end conversion. Even

at activation times of more than 40 minutes the catalyst is fully active and the end conversion is on target.

Table 6: Conversion data at 60, 100 and 180 minutes as a function of the activation time using 1 ppm of titanium on cement

Example	act. time (min)	60 min conv. (wt%)	100 min conv. (wt%)	180 min conv. (wt%)
19	1	37	69	97.5
20	5	43	91	98.5
21	10	46	97	99.1
22	20	50	95	99.1
23	42	42	88	97.5

Example 24 Hydrogenation of SBS block copolymer with Cp_2TiCl_2 . The catalyst intermediate was produced in a hydrogen free atmosphere.

A stainless steel reactor was charged with 800 grams of SBS cement, prepared as described in Example 1. The temperature of the reactor was fixed at 50 °C. In the experiment 4.2 mg of Cp_2TiCl_2 was applied. After an activation time of 10 minutes at 50 °C and 0.1 MPa of nitrogen, 85 per cent of the remaining LiH was neutralised by reaction with ethanol. The reactor was pressurised with hydrogen and the hydrogenation was allowed to run at 70 °C. The results are shown in Table 7 and Figure 6.

Example 25-26 Hydrogenation of SBS block copolymer with Cp_2TiCl_2 . The catalyst was aged for 4 hours at 50 °C in a hydrogen free atmosphere.

Following the same procedure as in example 24, two more experiments were carried out. In both experiments the activated catalyst was aged for four hours at 50 °C

under 0.1 MPa of nitrogen. In example 25 the remaining LiH was neutralised by reaction with ethanol after 10 minutes activation. In example 26 the ethanol was added after four hours. So an excess of LiH was present during the ageing period! After the four hours ageing the reactor was pressurised with hydrogen and the hydrogenation experiments were allowed to run at 70 °C. The results of both experiments are shown in Table 7 and Figure 6.

Both aged catalysts under a nitrogen atmosphere show a similar reactivity (examples 25 and 26), somewhat lower than the comparative example 24 in which the catalyst was not aged. Still good end conversions were reached after 3 hours of hydrogenation.

Table 7: Catalyst activity after 4 hours ageing at 50 °C

Example	EtOH addition	ageing time (hours)	Atmosphere During ageing	40 min conv. (wt%)	100 min conv. (wt%)	180 min conv. (wt%)
24	after activation	0	-	49	98	99
25	after activation	4	0.1 MPa N ₂	28	93	97
26	after 4 hours	4	0.1 MPa N ₂	30	96	97
C-27	after 4 hours	4	2.0 MPa H ₂	22	40	55

Comparative Example 27 Hydrogenation of SBS block copolymer with Cp_2TiCl_2 . The catalyst was aged for 4 hours at 50 °C under 2.0 MPa of hydrogen.

Following the same procedure as in example 24, the activated catalyst was aged for 4 hours at 50 °C under 2.0 MPa of hydrogen, before the ethanol was added. So an excess of LiH was present during the ageing period! After the four hours ageing the hydrogen pressure was raised to 5.0 MPa and the hydrogenation experiments were allowed to run for 3 hours at 70 °C. The results are shown in Table 7 and Figure 7.

Four hours ageing at 50 °C under 2.0 MPa hydrogen gave severe catalyst decay of the activated catalyst and the hydrogenation performance is poor, giving only 55 per cent conversion of olefinic bonds after 3 hours of hydrogenation.

Example 28-31 Hydrogenation of SBS block copolymer with Cp_2TiCl_2 . The catalyst was activated in a hydrogen free atmosphere at different temperatures.

A stainless steel reactor was charged with 800 grams of SBS cement, prepared as described in Example 1. In the experiments 4.2 mg of Cp_2TiCl_2 was applied. After an activation time of 10 minutes at various temperatures, 70 per cent of the remaining LiH was neutralised by reaction with ethanol. The hydrogenation was carried out at 70 °C. The results are shown in Table 8 and Figure 8.

Table 8: Conversion data as function of the activation temperature

Example	activation temperature (°C)	20 min conv. (wt%)	40 min conv. (wt%)	100 min conv. (wt%)
28	50	29	69	96
29	60	27	60	97
30	70	29	62	97
31	90	27	59	97

Example 32-36 Hydrogenation of SBS block copolymer with Cp_2TiCl_2 . The LiH was neutralised by reaction with various neutralising agents.

A stainless steel reactor was charged with 800 grams of SBS cement, prepared as described in Example 1. In the experiments 4.2 mg of Cp_2TiCl_2 was applied. After an activation time of 10 minutes at 70 °C, 70 per cent of the remaining LiH was consumed by the neutralising agents listed in Table 9. The hydrogenation was carried out at 70 °C. The results are shown in Table 9.

Table 9: Conversion data as a function of the applied neutralising agent

Example	compound c	30 min conv. (wt%)	60 min conv. (wt%)	180 min conv. (wt%)
32	-	7	8	8
33	ethanol	48	98	99
34	isopropanol	47	97	98
35	acetone	37	66	77
36	Ionol CP(a)	38	79	93

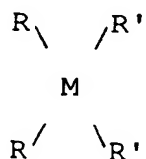
(a) Ionol CP is 2,6-ditertbutyl-4-methylphenol

C L A I M S

1. A method for preparing a hydrogenation catalyst system involving the reaction of a group 4 metallocene (A) with a metal hydride or an organometallic compound (B) at a (B)/(A) molar ratio that is larger than 10 followed by the activation of the resulting catalyst mixture with hydrogen at a hydrogen pressure p (in MPa) and at a temperature T (in °C), wherein a neutralising agent (C) that is capable of reacting with the compound (B) is added to the catalyst mixture -

- a) either prior to the activation, or
- b) within t hours from the activation wherein t equals x divided by (p * T * (B)/(A)), and x corresponds to 10,000.

2. A method as claimed in claim 1, wherein the group 4 metallocene is a compound represented by the following general formula:



in which each R represents the same or a different substituted or unsubstituted, fused, and/or heterocyclic cyclopentadienyl-like η^5 ligand; each R' represents the same or a different group selected from C₁-C₁₂ hydrocarbyl groups, C₁-C₁₂ hydrocarboxyl groups, a carbonyl group, a beta-diketone coordination group or -preferably- a halogen atom, and M is a titanium, zirconium or hafnium atom, preferably a titanium atom.

3. A method as claimed in claim 1 or 2, wherein the metallocene is bis(cyclopentadienyl)titanium dichloride.

4. A method as claimed in claims 1 to 3, wherein compound (B) is a lithium compound or a lithium hydride.

5. A method as claimed in claim 1 to 4, wherein the (B)/(A) ratio is larger than 15, preferably in the range of 20 to 500.

6. A method as claimed in claim 1 to 5, wherein the neutralising agent (C) is selected from ketone compounds, sulphoxide compounds, carboxylic acid compounds, carboxylate ester compounds, aldehyde compounds, lactone compounds, lactam compounds, amine compounds, amide compounds, nitrile compounds, epoxy compounds and oxime compounds, and is preferably ethanol.

7. A method as claimed in claim 1 to 6, wherein the neutralising agent (C) is used in a ratio of (C)/(B) in the range of 0.4 to 1.05, more preferably in a range of 0.45 to 1.0, e.g., most preferably in the range of 0.5 to 0.9, say in an amount of about 0.6.

8. A method as claimed in claim 1 to 7, wherein the neutralising agent (C) is added within t hours from contacting the catalyst mixture with hydrogen, wherein t is calculated based on x being 7,500, preferably 5,000.

9. A method as claimed in claim 1 to 7, wherein the neutralising agent (C) is added before contacting the catalyst mixture with hydrogen.

10. A process for the hydrogenation of an olefinically unsaturated compound with hydrogen in the presence of a hydrogenation catalyst system obtained by the method described in claims 1 to 9.

11. A process as claimed in claim 10, performed at partial hydrogen pressures in the range of from 0.1 to 10 MPa, and preferably from 0.1 to 5.0 MPa.

12. A process as claimed in claim 10 to 11, wherein the metallocene is used in amounts of from 0.1 to 500, typically from 1 to 100 mg per kg of unsaturated

compound, and preferably in amounts in the range of from 5 to 50 mg/kg.

- 5 13. A process as claimed in claim 10 to 12, wherein the unsaturated compound is a polymer, preferably a polymer of conjugated dienes such as 1,3-butadiene and/or isoprene and copolymers (random or block) of these dienes with vinylaromatic monomers, e.g. with styrene.

1/4

Fig.1.

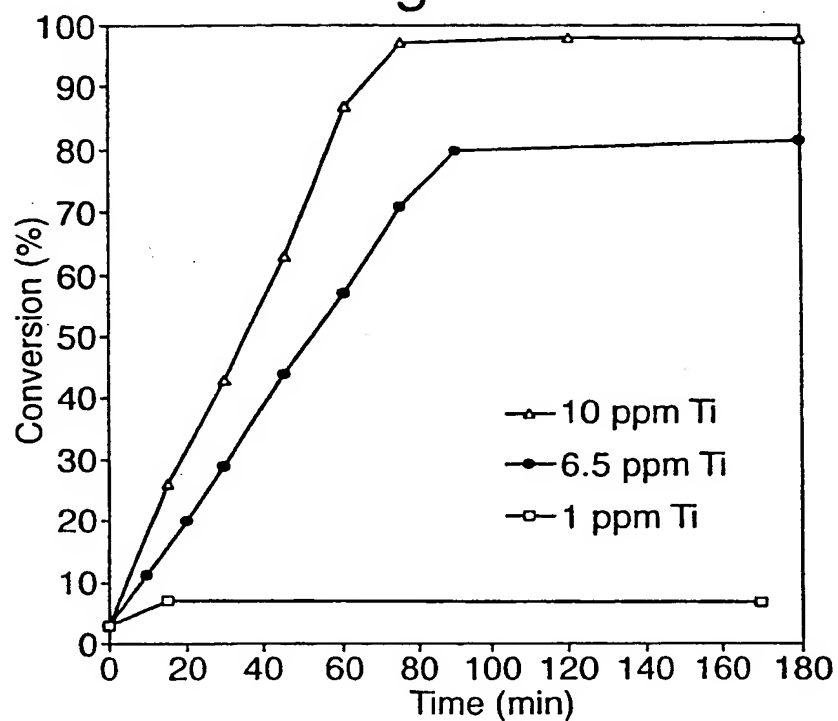
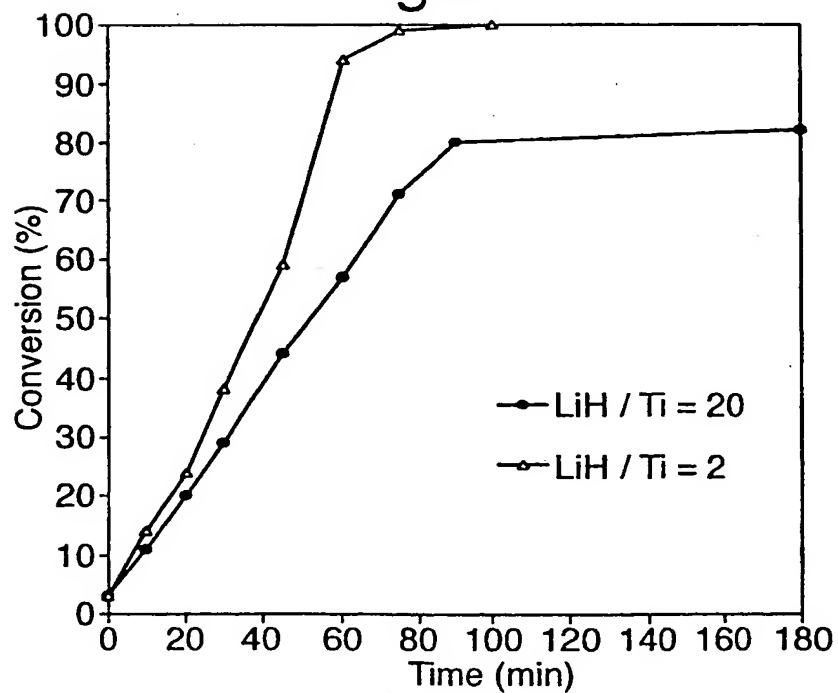


Fig.2.



2/4

Fig.3.

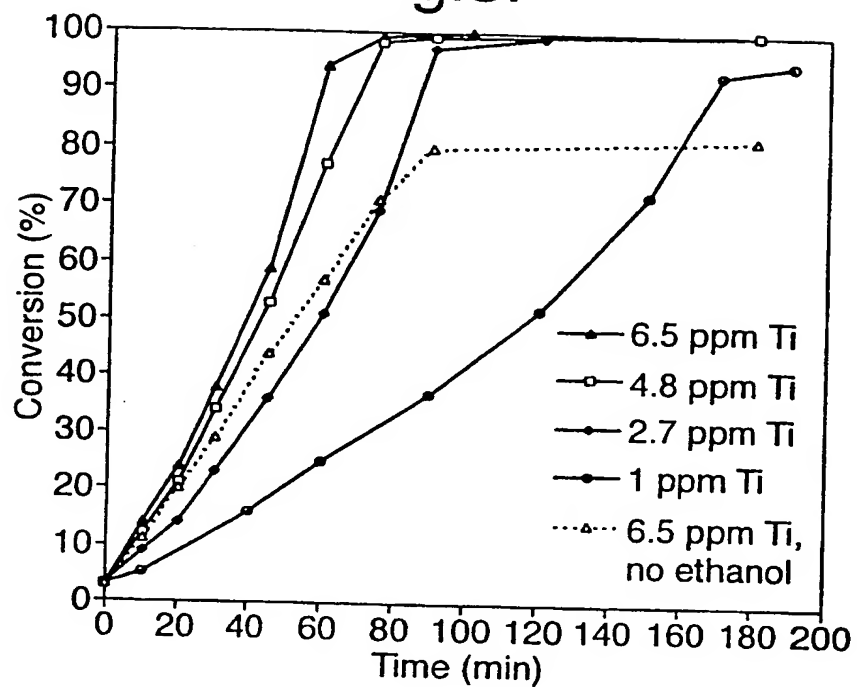
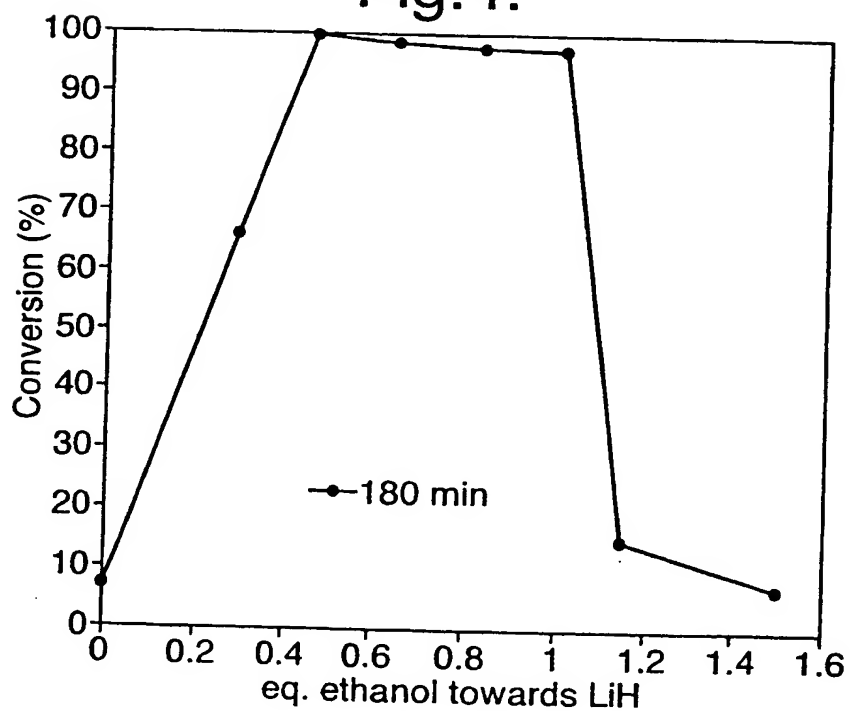


Fig.4.



3/4

Fig.5.

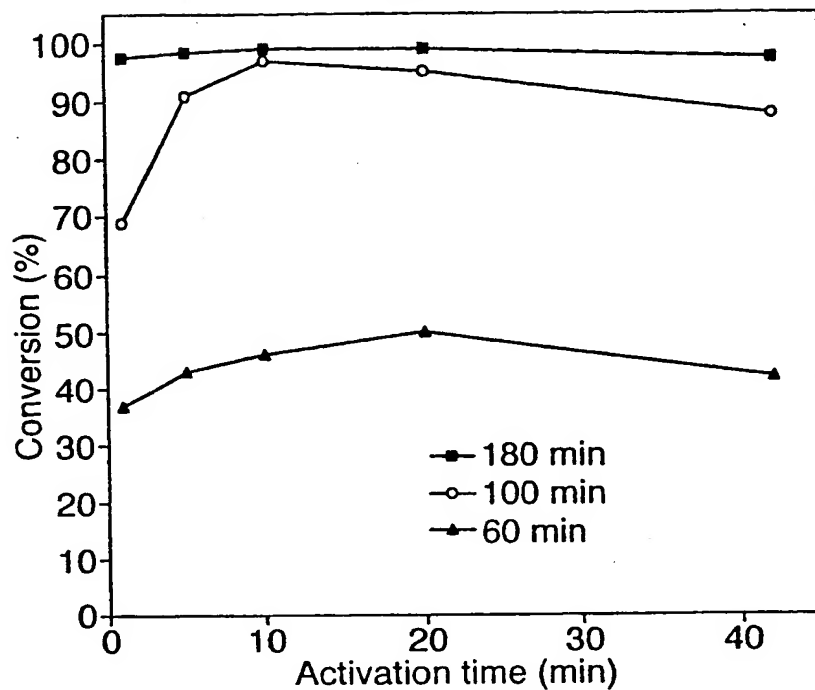
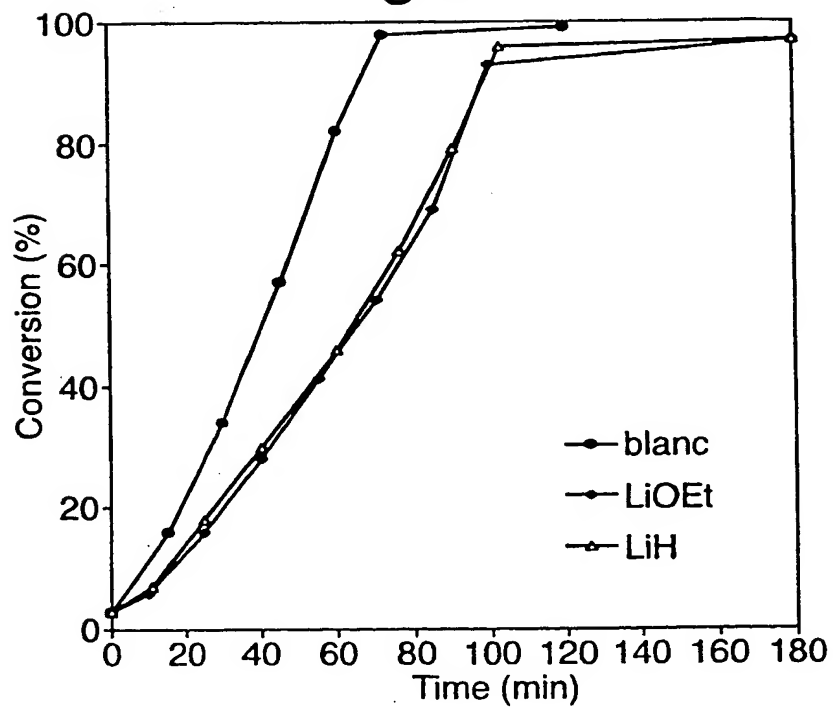


Fig.6.



4/4

Fig.7.

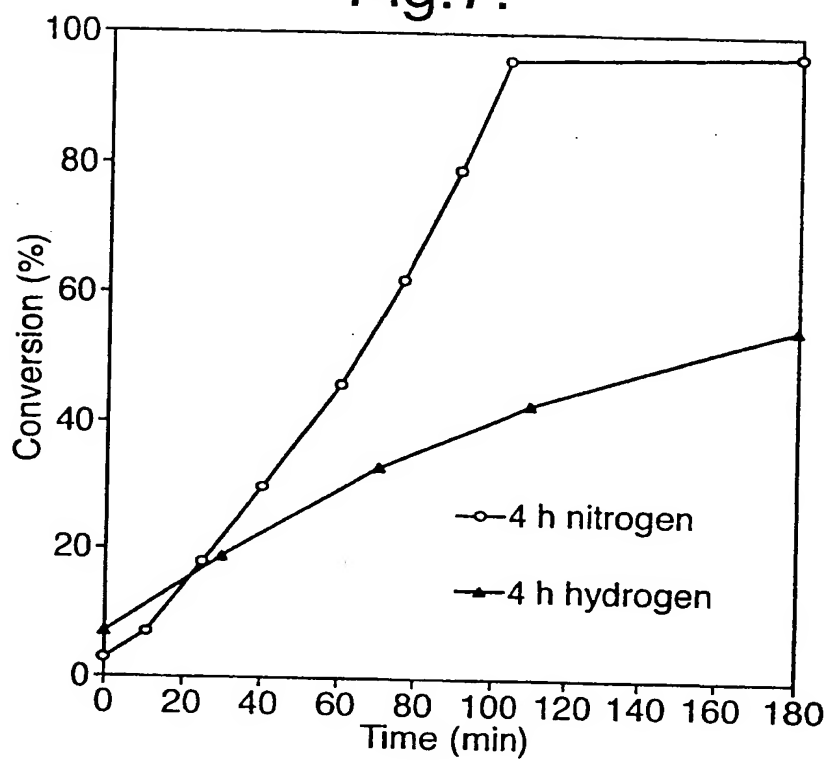
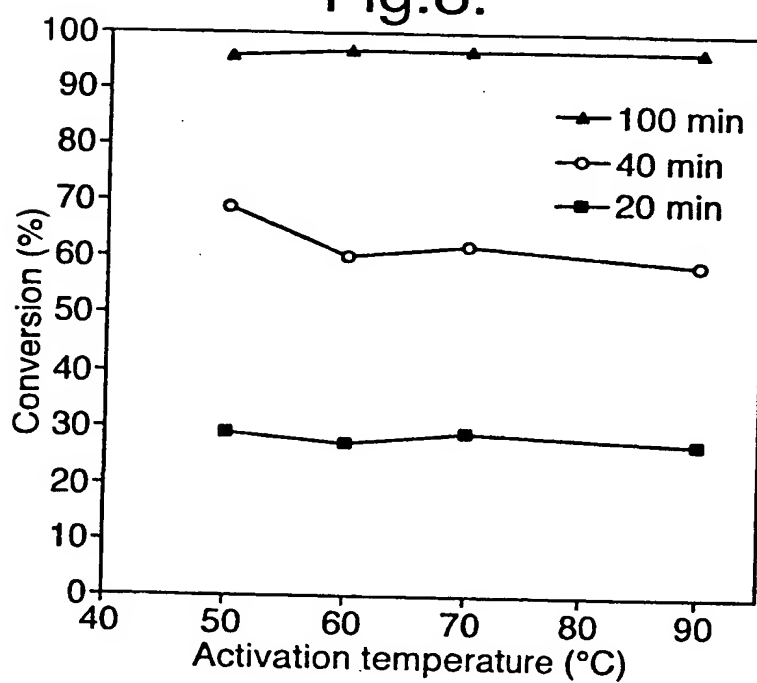


Fig.8.

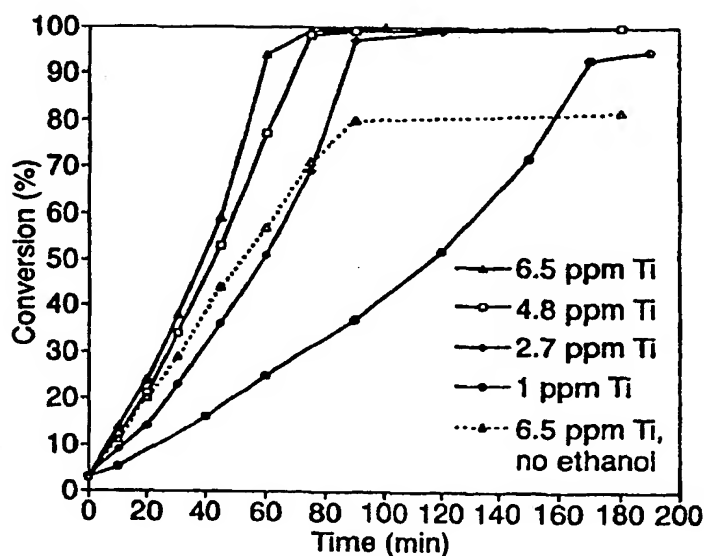




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷: B01J 31/12, 31/22, 37/04, C08F 8/04, C08C 19/02	A3	(11) International Publication Number: WO 00/25915 (43) International Publication Date: 11 May 2000 (11.05.00)
(21) International Application Number: PCT/EP99/08311 (22) International Filing Date: 28 October 1999 (28.10.99) (30) Priority Data: 98308932.7 30 October 1998 (30.10.98) EP (71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventors: VAN DER HEIJDEN, Harry; Badhuisweg 3, NL-1031 CM Amsterdam (NL). VAN DE WEG, Hendrik; Badhuisweg 3, NL-1031 CM Amsterdam (NL).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> (88) Date of publication of the international search report: 10 August 2000 (10.08.00)

(54) Title: A METHOD FOR PREPARING A HYDROGENATION CATALYST SYSTEM



(57) Abstract

This invention concerns a method for preparing a hydrogenation catalyst system process involving the reaction of a group 4 metallocene (A) with a metal hydride or an organometallic compound (B) at a (B)/(A) molar ratio that is larger than 10 followed by the activation of the resulting catalyst mixture with hydrogen at a hydrogen pressure p (in MPa) and at a temperature T (in °C), wherein a neutralising agent (C) that is capable of reacting with the compound (B) is added to the catalyst mixture: (a) either prior to the activation; b) within t hours from the activation wherein t equals x divided by $(p * T * (B)/(A))$, and x corresponds to 10,000, and a process for the hydrogenation of an olefinically unsaturated compound with hydrogen in the presence of a hydrogenation catalyst system obtained by the method of the invention.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

INTERNATIONAL SEARCH REPORT

Intern al Application No

PCT/EP 99/08311

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J31/12 B01J31/22 B01J37/04 C08F8/04 C08C19/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C08F C08C C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP 0 974 602 A (JSR CORP) 26 January 2000 (2000-01-26) the whole document	1,2,4,6, 10,11,13
A	US 5 173 537 A (CHAMBERLAIN LINDA RAE ET AL) 22 December 1992 (1992-12-22) cited in the application	
A	EP 0 434 469 A (JAPAN SYNTHETIC RUBBER CO LTD) 26 June 1991 (1991-06-26) cited in the application	
	-/-	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

8 May 2000

Date of mailing of the international search report

17/05/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Zuurdeeg, B

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/08311

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 199615 Derwent Publications Ltd., London, GB; Class A12, AN 1996-146206 XP002042426 & JP 08 033846 A (ASAHI KASEI KOGYO KK), 6 February 1996 (1996-02-06) cited in the application abstract</p> <p style="text-align: center;">-----</p>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/08311

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0974602 A	26-01-2000	JP 2000037632 A	08-02-2000
US 5173537 A	22-12-1992	BR 9205044 A	22-06-1993
		CN 1073687 A, B	30-06-1993
		DE 69206590 D	18-01-1996
		DE 69206590 T	15-05-1996
		EP 0549063 A	30-06-1993
		ES 2080435 T	01-02-1996
		JP 5239126 A	17-09-1993
		MX 9207381 A	01-07-1993
EP 0434469 A	26-06-1991	JP 2969771 B	02-11-1999
		JP 3223305 A	02-10-1991
		DE 69017164 D	30-03-1995
		DE 69017164 T	29-06-1995
		US 5169905 A	08-12-1992
JP 8033846 A	06-02-1996	NONE	